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The shell of the Great Scallop *Pecten maximus* as a high frequency archive of paleoenvironmental change

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Abstract

We investigate the environmental and biological controls on oxygen isotope ratios in the shells of modern *Pecten maximus* bivalves collected alive in the bay of Brest (France). Seasonal $\delta^{18}\text{O}$ profiles obtained by drilling the daily calcite ridges deposited at the surface of the left valve were compared with in situ measurements of temperature and salinity. We show that *P. maximus* $\delta^{18}\text{O}$ values accurately track seasonal variations in bottom water temperature. Shell growth rate has no significant effect on shell $\delta^{18}\text{O}$ values. Our study demonstrates that daily variations in water temperature can be reconstructed within about 0.5°C. Temperatures estimated with the paleotemperature equation established in this study, were compared with temperatures derived from previously published equations. The comparison indicates that the most commonly used paleotemperature equation for biogenic calcite [Epstein *et al.*, 1953] provides inaccurate temperature estimates, but the Kim and O'Neil [1997] equation, established from abiogenic calcite precipitation, provides results very similar to ours, and should therefore be used for scallop individuals coming from populations where proper empirical calibration cannot be done. *Pecten maximus* bivalves precipitate calcite in isotopic equilibrium with seawater, produce large daily growth striae, are stenohaline and are well preserved in archeological and geological deposits making them an excellent high frequency archive of paleoenvironmental change.

Keywords: bivalve; biogenic calcite; isotopes; oxygen; shell growth rate; temperature

1. Introduction

Knowledge of past natural environmental variation is a prerequisite for understanding possible future changes in a warming world. Environmental variables such as ocean temperature and salinity have not been directly measured except during the relatively short instrumental period. The chemical and isotopic composition of biologically-produced calcite and aragonite from mollusks and corals can provide proxy records of past and present environmental conditions and thus allow the reconstruction of environmental history. The known spatial heterogeneity of climate system responses to changes in radiative forcings suggests the need for near-global archives of pre-instrumental change. In addition, to make the reconstruction of past environmental conditions as reliable as possible, recorders from wide taxonomic and ecological ranges should be used. Accordingly, efforts are being made to acquire new environmental time series by using the skeletons of marine invertebrates ranging from the poles to the tropics.

The oxygen isotopic composition ($^{18}\text{O}/^{16}\text{O}$) of most marine carbonate is controlled by both the temperature and oxygen isotopic composition of the ambient sea water from which it is precipitated [Urey, 1947; Epstein *et al.*, 1953; Grossman and Ku, 1986]. The isotopic paleotemperature method has been utilized in a number of studies of Holocene and older mollusks [William *et al.*, 1982; Bice *et al.*, 1996, Andreasson and Schmitz 1996, 1998, 2000; Purton *et al.*, 1999, Kirby *et al.*, 1998, Kirby, 2001, Schmitz and Andreason, 2001; Goodwin *et al.*, 2004]. Analysis of mollusk carbonate provides information for small windows of time, yet these measurements can offer valuable insights into paleoclimate that serve as benchmarks for models of ancient climate and ocean circulation. One notable advantage of molluscan paleoclimate records is the preservation of seasonal variability of $\delta^{18}\text{O}$ within accretionary growth structures [Jones *et al.*, 1983, Dettman *et al.*, 1999; Dutton *et al.*, 2002; Elliot *et al.*, 2003]. Paleotemperature analysis using mollusks is often considered straightforward by virtue of a longstanding presumption that they precipitate carbonate minerals in isotopic equilibrium with seawater. Other carbonate paleoenvironmental archives, such as corals and many foraminiferal species, are known to precipitate carbonate with isotopic ratios that are significantly out of equilibrium with ambient conditions [Weber and Woodhead, 1972; Dunbar and Wefer, 1984, Spero *et al.*, 1997]. In fact, some bivalve species appear to precipitate their shell carbonate at or near isotopic equilibrium [Surge *et al.*, 2001; Elliot *et al.*, 2003] while others do not [Mitchell *et al.*, 1994; Owen *et al.*, 2002a,b], suggesting that

taxa-specific assessments must be completed. Difficulties and misunderstandings also arise from a lack of knowledge of the basic biology and ecology of the molluscan species used as environmental recorders. In particular, growth rate and the seasonal timing and duration of growth must be well-known [Ivany *et al.*, 2003]. Goodwin *et al.* [2003] demonstrate that growth cessations and/or changing growth rates can reduce the range of resolution of the recorded environmental conditions. Furthermore, isotopic paleotemperature reconstruction can be prone to large errors when using euryhaline bivalves, due to large uncertainties in $\delta^{18}\text{O}$ of the water [e.g., Gillikin *et al.*, in press]

In this paper we describe the calibration of the relationship between oxygen isotopic composition and temperature in a population of wild scallops in the Bay of Brest (France). $\delta^{13}\text{C}$ results are published in a companion paper [Lorrain *et al.*, 2004]. The biology of scallops in the Bay of Brest is well understood in terms of growth rate, reproduction, and energy allocation [Paulet *et al.*, 1988; Chauvaud *et al.*, 1996; Grall *et al.*, 1996; Paulet *et al.*, 1997; Chauvaud *et al.*, 1998; Saout *et al.*, 1999; Lorrain *et al.*, 2000; Chauvaud *et al.*, 2001; Lorrain *et al.*, 2002]. Scallops offer good opportunities for documenting past environmental conditions [Davenport, 1938; Hickson *et al.*, 1999; Owen *et al.*, 2002a,b] because their outer shell layer is composed of pure foliated calcite [Roux *et al.*, 1990; Barbin *et al.*, 1991] and they are relatively immune to dissolution and recrystallization. Like other non-motile benthic invertebrates, the great scallop, *Pecten maximus* is a potential eulerian sensor of its aquatic environment [Owen *et al.*, 2002a, b; Chauvaud *et al.*, submitted]. This scallop is perhaps the most useful of all the pectinids for paleoclimate studies because of its longevity (up to 12 years), high growth rate (up to 350-400 $\mu\text{m d}^{-1}$), stenohaline nature (and hence exposure to a reduced range in $\delta^{18}\text{O}_{\text{water}}$), and production of both seasonal and daily growth bands [Chauvaud *et al.*, 1998]. Today, *P. maximus* has a wide geographical range and is abundant from southern Agadir (Morocco) to the Lofoten Islands (Norway), and occurs in the Mediterranean Sea (Malaga) and all along the French, Irish, and Scottish coasts. Shells of *P. maximus* are commonly found in sediments from these regions.

Scallops are typically fast-growing, facilitating the analysis of environmental conditions over short time steps. We have previously shown that *P. maximus*, like other pectinids, produce daily lamellae on the left valve [see Chauvaud *et al.*, 1998]. By counting lamellae to establish a Julian day chronology for *P. maximus* from the Bay of Brest we demonstrated (1) a complete winter cessation in growth, (2) a pronounced seasonal variation in daily growth rate,

and (3) independence between growth rate and food availability, suggesting that temperature is the main factor regulating shell growth rate. This understanding of shell growth dynamics enhances our ability to develop and accurately calibrate useful paleoenvironmental tracers for this organism. In this paper, we examine the oxygen isotopic composition of carbonate collected along growth transects from multiple specimens of *P. maximus* and develop a temperature calibration using in-situ temperature and salinity data. This new calibration is compared to several different published paleotemperature equations in order to test whether the carbonate was deposited in isotopic equilibrium. We consider both growth rate and temperature effects when assessing the adherence to oxygen isotopic equilibrium.

2. Materials and methods

2.1. Study site

The Bay of Brest (Figure 1) is a semi-enclosed marine ecosystem of $\sim 180 \text{ km}^2$ connected to shelf waters by a narrow (2 km wide) and deep (40 m) strait. The bay is a shallow basin with 50% of its area shallower than 5 m (average depth 8 m). There are five watersheds responsible for freshwater inputs to the bay, but those from the two main rivers, the Aulne (1842 km^2) and the Elorn (402 km^2) make up 80% of the total freshwater input. Tidal action induces short term variability in hydrographic parameters and mixing of water masses [see *Quéguiner and Tréguer*, 1984; *Salomon and Breton*, 1991]. Tidal variation reaches 8 m during spring tides, resulting in an oscillating volume that is 40% of the high tide volume. Our study site, the Roscanvel Bank (30 m deep), is characterized by mixed sandy and silty sediments and strong tidal flows [*Salomon and Breton*, 1991]. The Bay of Brest is a marine system, since in winter; bottom water salinity decreases only from ~ 35 to ~ 32.5 at station R3 during flood tide. During spring through autumn, when *P. maximus* is accreting carbonate, salinity is quite stable [bottom water salinity = 34-35; *Chauvaud et al.*, 1998].

2.2. Environmental parameters

Bottom water temperature and water column salinity were monitored for several years at station R3 (Figure 1). Bottom water temperature was measured every 30 minutes using an EBRO Ebi-85 thermal probe fixed to a bottom mooring (precision = 0.1°C). In the water column, salinity (conductivity precision = 0.001S/m) and temperature (precision = 0.01°C) were recorded using a SeaBird SBE19 CTD profiler. CTD measurements were collected over different time scales, ranging from daily measurements during algal bloom periods to monthly

measurements during winter. Seawater samples were collected at 11 locations along a salinity gradient from fresh to marine water (Elorn estuary; Figure 1) during March 2001 for the measurement of $\delta^{18}\text{O}_{\text{water}}$ (precision = 0.04‰). Salinities were also determined in order to establish the relationship between local salinity and seawater $\delta^{18}\text{O}$.

2.3. Scallop sampling and shell growth rates

Live scallops were collected from Roscanvel bank (Figure 1) using SCUBA or using a dredget equipped with metallic rings 55 mm in diameter. As previously described by *Dillon and Clark* [1980], *P. maximus* has two different types of external growth lines: (i) the “annual winter rings” (Figure 2), reflecting a period of very slow growth or complete growth cessation during the winter months, which provides an accurate tool for the determination of age for each individual [*Mason*, 1957; *Grall et al.*, 1996; *Boucher and Fifas*, 1997; *Thouzeau et al.*, 2000]; and (ii) the broader and darker rings representing fast growth period during the rest of the year. Acute examination of the broader rings reveals the presence of very thin concentric structure attested as daily growth increments [*Chauvaud et al.*, 1998, *Lorrain et al.*, 2000, 2004].

For isotopic analyses, individuals of age class I (showing 1 winter mark on the shell, N=10) were sampled in late December of each year (i.e., after the growing season but before the “winter” mark deposit). Age I scallops were chosen because they have the longest annual growth season, and thus accumulate the longest annual calcitic record (i.e., between the first and the second winter, Figure 2). To build the paleotemperature equation, 7 scallops were used (3 sampled in 1994, 3 in 1995 and 1 in 1996); then to validate the equation, 3 more shells were sampled in late 2000 (shells A, B and C). Daily growth rate was determined by measuring distances between successive daily growth striae on the left valve using the image analysis method described in *Chauvaud et al.* [1998]. Each year, the date of growth restart and subsequently the absolute dating of calcitic increments, was determined by counting and measuring the daily increments from the ventral edge to the first winter mark on juveniles sampled in July-August, i.e. during the growth period; based on the daily rhythm of striae deposit, absolute dates are thus assigned to each striae by backdating from the last striae (collection date). The mean daily growth is calculated for all individuals sampled during summer. This growth rate series is then used as reference to assign dates to the striae from the specimens collected after the growing season by minimizing the sum of the differences between the two series [*Walter and Pronzato*, 1994]. Each calcitic sample for the

$\delta^{18}\text{O}_{\text{calcite}}$ /temperature calibration therefore has a very precise calendar date. Temperature data were averaged to the corresponding time sampled from the shell.

2.4. $\delta^{18}\text{O}_{\text{calcite}}$

Samples for isotopic analysis were obtained using a small drill with a 0.3-mm engraving bit. Because both rate and duration (number of days) of growth decrease during the ontogeny of *P. maximus* [Chauvaud, 1998], all shells were sampled between the first and the second winter mark (Figure 2) by drilling small grooves parallel to growth bands at approximately 1- to 2-day intervals along a sampling transect from oldest to youngest material in the calcitic outer layer of the shell. Each groove is cut to a depth shallower than 150 μm in order to ensure that the powder sample is not collected from different layers of calcite deposition. Aliquots of *P. maximus* calcite weighing between 18 and 95 μg (mean: 69 μg) were acidified in 100% phosphoric acid at 70°C for 470 s and analyzed using an automated Finnigan MAT Kiel III carbonate device coupled to a Finnigan MAT 252 isotope ratio mass spectrometer at Stanford University. A total of 381 unknown samples were analyzed with a replication rate of 3.4%. 86 NBS-19 (National Institute of Standards and Technology, NIST SRM 8544) standards were analyzed along with the shell samples. The regular analysis of NBS-19 during this study yielded a standard deviation of 0.059‰ for $\delta^{18}\text{O}$. In addition, 279 analyses of the Stanford Isotope Lab Standard SLS-1 were analyzed during this study, with a standard deviation of 0.065‰ for $\delta^{18}\text{O}$. All isotope data are expressed in the conventional delta (δ) notation,

$$\delta \text{‰} = ((\text{Ratio sample} - \text{Ratio reference}) / (\text{Ratio reference})) * 1000 \quad (1)$$

where the isotope ratios of $^{18}\text{O}/^{16}\text{O}$ are reported relative to the international VPDB (Vienna Pee Dee Belemnite) standard.

2.5. $\delta^{18}\text{O}_{\text{water}}$

The $\delta^{18}\text{O}$ of water samples have been analysed by the accepted procedure of equilibration with a head-space of carbon dioxide [McMillan *et al.*, 1989]. A sample size of 0.3 ml was placed in a septum-sealed container (Labco, High Wycombe, UK) and flushed for 2 minutes with carbon dioxide. Samples and standards were allowed to equilibrate at room temperature for at least 24 hours prior to analysis. The head-spaces in the containers were then analysed on a continuous flow - isotope ratio mass spectrometer (ANCA-GSL/Geo 20-20, Europa Scientific, Crewe, UK). Data were normalized to an internal laboratory water standard and

absolute values are referenced relative to VSMOW (Vienna standard mean ocean water). Each sample and reference was analyzed in triplicate. The long-term reproducibility of triplicate analysis in this laboratory is routinely < 0.2 ‰. However, the average standard deviation of our triplicate sample analyses was < 0.1 ‰.

2.6. $\delta^{18}\text{O}_{\text{calcite}}$ - Temperature Relationship

Historically, the $\delta^{18}\text{O}_{\text{calcite}}$ - temperature relationship for calcite has been determined by two different means:

(1) Empirical equations derived from isotopic measurements of shells from mollusks grown at several different temperatures [e.g., *Epstein et al.*, 1953 later modified by *Craig*, 1965].

$$T(^{\circ}\text{C}) = 16.9 - 4.2 (\delta^{18}\text{O}_{\text{calcite}} - \delta^{18}\text{O}_{\text{water}}) + 0.13 (\delta^{18}\text{O}_{\text{calcite}} - \delta^{18}\text{O}_{\text{water}})^2 \quad (2)$$

Both $\delta^{18}\text{O}_{\text{calcite}}$ and $\delta^{18}\text{O}_{\text{water}}$ in this equation are relative to the same working standard, CO_2 from PDB, and corrections have to be made as $\delta^{18}\text{O}_{\text{water}}$ is nowadays given on the VSMOW scale [see *Bemis et al.*, 1998]. Therefore, this equation has been rewritten by *Anderson and Arthur* [1983] to be expressed relative to commonly used international standards, i.e., VPDB and VSMOW:

$$T(^{\circ}\text{C}) = 16 - 4.14 (\delta^{18}\text{O}_{\text{calcite}} - \delta^{18}\text{O}_{\text{water}}) + 0.13 (\delta^{18}\text{O}_{\text{calcite}} - \delta^{18}\text{O}_{\text{water}})^2 \quad (3)$$

where $\delta^{18}\text{O}$ values of calcite ($\delta^{18}\text{O}_{\text{calcite}}$) are relative to the VPDB standard and $\delta^{18}\text{O}$ values of water ($\delta^{18}\text{O}_{\text{water}}$) are relative to the VSMOW standard. Equations 2 and 3 are therefore statistically same.

(2) Empirical equations derived from isotopic measurements of inorganically precipitated calcite. *O'Neil et al.* [1969] proposed the following equation, derived from experiments over the temperature range 0-500°C:

$$1000 \cdot \ln \alpha_{\text{calcite-water}} = 2.78(10^6 T^{-2}) - 2.89 \quad (4)$$

where T is the temperature in K and α is the isotope fractionation factor ($\alpha_{\text{calcite-water}}$):

$$\alpha_{\text{calcite-water}} = \frac{1000 + \delta^{18}\text{O}_{\text{calcite}}}{1000 + \delta^{18}\text{O}_{\text{water}}} \quad (5)$$

The $\delta^{18}\text{O}$ values of both calcite ($\delta^{18}\text{O}_{\text{calcite}}$) and water ($\delta^{18}\text{O}_{\text{water}}$) in the above equation are relative to the VSMOW standard whereas our own values for calcite and water are expressed relative to VPDB and VSMOW respectively. For comparison purposes, we convert our

P. maximus $\delta^{18}\text{O}_{\text{VPDB}}$ values to $\delta^{18}\text{O}_{\text{VSMOW}}$ using the following expression [Coplen *et al.*, 1983]:

$$\delta^{18}\text{O}_{\text{VSMOW}} = 1.03091 \cdot \delta^{18}\text{O}_{\text{VPDB}} + 30.91 \quad (6)$$

Equations 3 and 4 are essentially indistinguishable from each other, in the limits of experimental uncertainties, at least over the temperatures at which bivalves usually live and grow (8-20°C), leading to the idea that bivalves precipitate their shells in oxygen isotopic equilibrium with seawater.

Kim and O'Neil [1997] revisited the *O'Neil et al.* [1969] equation and proposed a new expression derived from experimental precipitation of synthetic calcite that is in good agreement with *O'Neil et al.* [1969] above 25°C, but shows a relatively large difference around 10°C [around 1.2°C; see Figure 1 in *Kim and O'Neil*, 1997]:

$$1000 \ln \alpha_{\text{calcite-water}} = 18.03(10^3 T^{-1}) - 32.42 \quad (7)$$

Kim and O'Neil [1997] also determined new mineral-specific acid fractionation factors for the analysis of $\delta^{18}\text{O}$ in carbonates. For calcite, they use a value of 1.01050 whereas all other publications (and our own work) incorporate an acid fractionation factor of 1.01025. We therefore subtract 0.25‰ from our measured $\delta^{18}\text{O}_{\text{calcite}}$ values when predicting temperature using their equation. For comparison purposes, *Bemis et al.*, [1998] have transformed equations 4 and 7 in the quadratic form $T(^{\circ}\text{C}) = a + b(\delta^{18}\text{O}_{\text{calcite}} - \delta^{18}\text{O}_{\text{water}}) + c(\delta^{18}\text{O}_{\text{calcite}} - \delta^{18}\text{O}_{\text{water}})^2$ where both $\delta^{18}\text{O}$ are relative to VPDB. However, in our study, we preferred to keep the original forms and to express $\delta^{18}\text{O}_{\text{water}}$ vs. VSMOW to avoid approximations and multiple corrections.

Our main goal is to develop an empirical calibration for wild *Pecten maximus* shells using in situ temperature and salinity data. To test whether wild scallops deposit calcite in isotopic equilibrium with seawater, we calculate the expected temperature under the equilibrium precipitation hypothesis using the *Kim and O'Neil* equation [1997, equation 7], and compare this to our empirically calculated temperature. We conduct a similar comparison using the equation of *Epstein et al.* [1953; equation 3] as it is often utilized for paleotemperature reconstructions using calcitic organisms [e.g., *Marshall et al.*, 1997; *Curry and Fallick*, 2002; and many others]. $\delta^{18}\text{O}_{\text{water}}$ values are calculated for each corresponding calcite sample using the observed $\delta^{18}\text{O}_{\text{water}}$ /salinity relationship.

3. Results

3.1. $\delta^{18}\text{O}_{\text{calcite}}$ variation in *Pecten maximus* and shell growth rate

Shell daily growth rate, $\delta^{18}\text{O}_{\text{calcite}}$, and temperature variations are superimposed in Figure 3. *P. maximus* precipitates calcite with a strong seasonal cycle in $\delta^{18}\text{O}$. Daily growth rate varies by over an order of magnitude within each of the scallops, from 10 to 350 $\mu\text{m d}^{-1}$. As previously observed, shell growth ceases during winter. During the growth period, the daily growth rate (DGR) exhibits non steady-state dynamic pattern with a sharp initial increase followed by a longer decrease. DGR trajectories converge asymptotically to an equilibrium described by a function of the seasonal evolution of light and temperature [Chauvaud *et al.*, submitted]. During toxic dinoflagellate bloom events, DGR drops to near zero [e.g., June-July 1995, Figure 3, Chauvaud *et al.*, 1998].

From these results, $\delta^{18}\text{O}_{\text{calcite}}$ appears to be correlated with temperature only. In particular, reduced growth in June and July 1995 does not affect $\delta^{18}\text{O}_{\text{calcite}}$. These results suggest that $\delta^{18}\text{O}_{\text{calcite}}$ variations follow water temperature and not the growth rate of the shell.

3.2. $\delta^{18}\text{O}_{\text{water}}$ versus Salinity

Water $\delta^{18}\text{O}$ values of samples collected along a 15-km transect between the Elorn River and the Bay of Brest exhibit a linear covariation with salinity over a wide range in salinity (0 to nearly 35). The relationship yields the following least-squares regression equation ($R^2 = 0.9998$, $n=11$, $p<0.0001$, Standard Error of Est. = 0.042):

$$\delta^{18}\text{O}_{\text{water (VSMOW)}} = 0.164 (\pm 0.001) S - 5.38 (\pm 0.02) \quad (8)$$

where S is salinity (Figure 4A). The intercept suggests that Elorn River water has a $\delta^{18}\text{O}_{\text{water}}$ value of - 5.38 ‰ relative to VSMOW.

Long time series of marine or river water isotopic composition are not available from the Bay of Brest region, so the extent to which the relationship described in equation 8 may be used for calibrating scallops growing between 1994 and 1996 must be considered. 56 precipitation samples collected at Brest/Plouzane between April, 1996 and December, 2000 yield a mean $\delta^{18}\text{O}_{\text{water (VSMOW)}}$ of -4.7‰ [IAEA/WMO, 2001], close to our estimated Elorn River end-member value of -5.4‰. The standard deviation of this set of monthly precipitation $\delta^{18}\text{O}$ values is 1.7‰. However, the standard deviation of the annual averages for each of the 5 years for which data is available is only ~0.5‰. We conclude that both seasonal and interannual variability in rainfall, and hence river water, $\delta^{18}\text{O}$ in the Bay of Brest region is

small, as expected given its predominantly maritime climate. Given the small freshwater dilution effect at Roscanvel Bank (over 30 years salinities have varied by <2) and the observation that both river and precipitation $\delta^{18}\text{O}$ values are typically within 5‰ of seawater values, we expect that interannual variability in the magnitude of the freshwater dilution effect on scallop $\delta^{18}\text{O}$ will be small (generally <0.05‰). The mean seasonal variation in salinity at Roscanvel Bank was calculated using 30 years of time series observations. Applying equation 8 we estimate a seasonal variability in $\delta^{18}\text{O}_{\text{water}}$ of $0.12 \pm 0.05\text{‰}$ (Figure 4B). This relationship is used to estimate values of $\delta^{18}\text{O}_{\text{water}}$ for calibration purposes.

3.3. Calibration of the temperature proxy

To build the paleotemperature equation, we used daily observed temperature, $\delta^{18}\text{O}_{\text{water}}$ calculated from observed salinity and *P. maximus* calcite $\delta^{18}\text{O}$ (Figure 5). The resulting linear relationship is:

$$T(^{\circ}\text{C}) = 14.84(\pm 0.06) - 3.75(\pm 0.1)(\delta^{18}\text{O}_{\text{calcite}} - \delta^{18}\text{O}_{\text{water}}) \quad (9)$$

($n = 333$, $R^2 = 0.92$, $p < 0.01$) over the in situ temperature range of 9 to 18°C, where T is the water temperature in °C, and $\delta^{18}\text{O}_{\text{calcite}}$ and $\delta^{18}\text{O}_{\text{water}}$ are expressed relative to VPDB and VSMOW respectively.

3.4. Validation

We analyzed 126 $\delta^{18}\text{O}_{\text{calcite}}$ samples from 3 scallops dredged in 2000 (A, B and C) at the same location as our calibration samples. $\delta^{18}\text{O}_{\text{calcite}}$ in these scallops follows the same pattern as observed during 1994-1996. Equation 9 was used to calculate seawater temperature from the $\delta^{18}\text{O}_{\text{calcite}}$ values and we compare these to temperatures derived from an in-situ probe. The temperatures determined from scallop $\delta^{18}\text{O}$ closely track bottom water temperatures (Figure 6). Using a linear model:

$$T_{\text{cal}} = 1.0045 T_{\text{obs}} \quad (10)$$

(multiple $R^2 : 0.98$; F-statistic: 8.10^4 on 1 and 125 DF, p-value < 0.00001)

The slope is not significantly different from 1 ($\text{Pr}(>[t])=0.196$). The measured mean temperature of the growth season (14.56°C from April to November) is indistinguishable from the estimated temperature of 14.63°C (95% confidence limits: 14.53 - 14.73°C). These results illustrate that we can use Equation 9 to evaluate water temperature variations at daily time resolution using $\delta^{18}\text{O}_{\text{calcite}}$ values from the shell of scallops. The standard error of the estimate shows the standard deviation of the residuals to be 0.53°C.

4. Discussion

The presence of daily growth banding in *Pecten maximus* and the amount of biological knowledge available for this species allows for a useful in-the-field paleotemperature calibration for the first time (equation 9).

4.1. Do *Pecten* precipitate at equilibrium?

Since the pioneering experimental work of *McCrea* [1950] and *Epstein et al.* [1953] various expressions describing partitioning of oxygen isotopes between calcite and water have been proposed [*Kim and O'Neil*, 1997, *Bemis et al.*, 1998, *Zeebe*, 1999, *Owen et al.*, 2002b]. We first examine *Kim and O'Neil's* [1997] equation using the pH of seawater as suggested by *Owen et al.* [2002b] to test whether this species precipitates its shells in isotopic equilibrium. Here, the high-resolution sampling reduces time averaging to the daily scale and allows evaluation of equilibrium precipitation of shell calcite.

By comparing measured $\delta^{18}\text{O}_{\text{calcite}}$ and predicted $\delta^{18}\text{O}_{\text{calcite}}$ using the equation of *Kim and O'Neil* [1997] we conclude that *P. maximus* precipitates calcite in equilibrium with seawater ($\Delta\delta^{18}\text{O} = -0.03 \pm 0.14\text{‰}$). We note that *Owen et al.* [2002b] published a paleotemperature equation for *P. maximus* showing a difference of 0.6‰ between predicted $\delta^{18}\text{O}_{\text{calcite}}$ (using the *Kim and O'Neil* [1997] equation) and their observed $\delta^{18}\text{O}_{\text{calcite}}$. Their study was performed under heavily manipulated experimental conditions at only four discrete experimental temperatures and their replicate data highlights significant inter-individual variation. In our work, we use a large dataset of $\delta^{18}\text{O}_{\text{calcite}}$ and temperature values representing a continuous natural range through the year. We therefore expect an improved fit for the linear relationship between temperature and $\delta^{18}\text{O}_{\text{calcite}}$.

In other words we conclude with confidence that wild *P. maximus* individuals precipitate their shells in equilibrium with seawater, when using *Kim and O'Neil* [1997] relationship to predict equilibrium values.

Figure 7 shows average predicted temperatures calculated using the *Kim and O'Neil* [1997, equation 7] and *Epstein et al.* [1953, equation 3] equations as well as our equation 9, compared to measured temperature. T estimates using our equation are very close to the observed values as well as those derived using *Kim and O'Neil* [1997], but are significantly less than those calculated using the equation of *Epstein et al.*, [1953] (by $\sim 1^\circ\text{C}$).

Kim and O'Neil [1997] argue that their equation is more robust than those previously published by *Epstein et al.* [1953] and *O'Neil et al.* [1969], because of the larger number of experiments performed, the large temperature range used, and the experimental conditions which produced only calcite. The close correlation of their equation determined for inorganic calcite precipitation and our own equation for biogenic carbonate argues for equilibrium isotopic precipitation in this species and suggests that their equation is in fact reliable for use in paleotemperature reconstructions from bivalve shells.

4.2. Growth influence

Previous studies have suggested that $\delta^{18}\text{O}_{\text{calcite}}$ values in mollusks are not only dependent on $\delta^{18}\text{O}_{\text{water}}$ and water temperature [*Epstein et al.*, 1953] but also on calcium carbonate precipitation rate [*McConnaughey*, 1989; *McConnaughey et al.*, 1997], taken here as the thickness of daily growth increments (termed shell growth rate in this study) as calcification rates are not easily measurable [see discussion in *Gillikin et al.*, 2005]. *Mitchell et al.* [1994] and *Owen et al.* [2002a, b] suggested kinetic isotope effects that are most prominent in fast growing shells of *P. maximus*. To test such hypotheses, we plot $\delta^{18}\text{O}_{\text{calcite}}$ versus temperature, salinity, and growth rate (Figure 8). In order to determine the influence of these three variables on $\delta^{18}\text{O}_{\text{calcite}}$ we use our data set to build a multivariate linear model fitting these variables to $\delta^{18}\text{O}_{\text{calcite}}$ (Table 1A). Considering that the P-value for $\delta^{18}\text{O}_{\text{water}}$ is 0.24 (i.e., P-value >0.05), this term is not statistically significant and the model can therefore be simplified. The best multiple linear regression model then incorporates only shell DGR and water temperature (Table 1B). However, in this adjusted linear model shell DGR explains only 0.5% of the variation in $\delta^{18}\text{O}_{\text{calcite}}$.

Results of the present study, carried out on a wild population of scallops demonstrate that shell growth rate (measured *a posteriori* at a daily scale) is not a governing factor influencing shell $\delta^{18}\text{O}_{\text{calcite}}$. Nevertheless, there is a statistical link between these two parameters. This link most likely evolves from a much more complex relationship between shell growth and water temperature. The growth of *P. maximus* juveniles of this species only takes place from early April to late November. During this period of metabolic activity, environmental conditions (photoperiod, temperature, food availability) control shell growth by modulating the size of each daily striae, but not as a steady-state process [*Chauvaud et al.*, submitted]. Then during a part of the year (Fall) shell growth rate and temperature co-vary and that's why a statistical

link appears in the multilinear model between shell growth rate and $\delta^{18}\text{O}_{\text{calcite}}$ (Table 1), even if it is clear from Figure 8 that this growth rate cannot explain much of the $\delta^{18}\text{O}_{\text{calcite}}$ variability.

These results contradict previously published data [Owen *et al.*, 2002a] showing a strong shell growth rate effect on scallop $\delta^{18}\text{O}$. However, we have noted above that Owen *et al.* reared scallops out of their ecological niche in their own study. *P. maximus* is a benthic species living in heterogeneous sediments and is sensitive to any abrupt variations in its environment [Chauvaud *et al.*, 1998, 2001; Lorrain *et al.*, 2000, 2002] as well as to any physical manipulation [Richardson, 1990]. We suggest that natural growth conditions alone allow for an accurate interpretation of the impact of shell growth in $\delta^{18}\text{O}_{\text{calcite}}$. Indeed, bivalve growth cessations and/or changing growth rates can reduce the range and the resolution of the recorded environmental conditions [Goodwin *et al.*, 2003]. In *Pecten maximus*, growth cessations and/or changing growth rates occurs after any type of manipulation (Chauvaud, unpublished) and a clearly visible growth check is formed in the shell after each handling [Richardson, 1990]. In addition, we have demonstrated here that when shell growth rates are reduced during a toxic dinoflagellate bloom [in June-July 1995, Figure 3; Chauvaud *et al.*, 1998], $\delta^{18}\text{O}_{\text{calcite}}$ variations still precisely follow temperature variations. It seems clear from the results of the present work and those performed earlier by Tarutani *et al.* [1969] and Kim and O'Neil [1997] that precipitation rate has little or no influence on the oxygen isotope fractionation between calcite and water during shell growth by this species.

4.3. Limits of the *Pecten* model

Because both geochemical and sclerochronological characteristics in bivalve shells reflect an individual's surroundings, these parameters are reliable indicators of environmental conditions. Both $\delta^{18}\text{O}_{\text{calcite}}$ values and daily growth-band widths provide valuable information about the annual growth of marine bivalves [Krantz *et al.*, 1984; Tan *et al.*, 1988; Goodwin *et al.*, 2001; Owen *et al.*, 2002b]. Our results demonstrate that accurate and precise high-resolution records of water temperature/ $\delta^{18}\text{O}_{\text{water}}$ may be obtained from *Pecten* calcite.

However, as previously demonstrated by Owen *et al.* [2002b] in *Pecten maximus* and by Hickson *et al.* [1999] in *Aequipecten opercularis*, the lowest water temperatures attained during the year are not recorded in the shell $\delta^{18}\text{O}$ record because the shell does not grow

during winter. Winter growth cessation is a common phenomenon in bivalves [Goodwin *et al.*, 2003] and winter temperatures cannot be reconstructed from many bivalve species.

Although predicted and observed temperatures show high correlation ($R^2=0.98$, equation 10), some inter-individual isotopic variability is observed (Figure 6). Indeed, the portion of shell A accreted in July and August is slightly enriched in ^{18}O relative to the two other individuals, showing that at the same time period, individuals can display slightly different $\delta^{18}\text{O}$ values. Such a difference has already been observed for $\delta^{13}\text{C}$ values [Lorrain *et al.*, 2004] from the same individuals (shells A, B and C). These authors proposed that an increase in shell $\delta^{13}\text{C}$ is caused by lower metabolic rates, i.e., a lower respiration to calcification ratio. Furthermore, in bivalves, calcification takes place in the extrapallial fluid [fluid lying between the mantle and the shell; Crenshaw, 1972] where strong biological controls can be expected. So, another possible explanation for the inter-individual variability reported in the present study may lie in differences in the chemistry of the extrapallial fluid between the three individuals.

One other limit of our calibration is the low number of replicates at the lowest temperatures. Because shell daily growth rate decreases with temperature, it is difficult to sample the calcite at daily resolution at low temperatures. The phenomenon leads to a differential smoothing of the temperature signal recorded by the shell (i.e., time averaging). For this reason, inter-individual variability is lower during period of low growth rate.

Finally, another limit of our calibration can be that scallops are not precipitating during the entire day [e.g., Wheeler *et al.*, 1975]. Therefore, the $\delta^{18}\text{O}$ value of daily growth striae might not be representative of the average daily temperature. This could be significant because strong tidal exchanges between the Bay of Brest and the adjacent Iroise Sea (Figure 1) can cause variations of an average of 1°C during the tidal cycle in summer [Chauvaud *et al.*, 1998]. More knowledge on the hourly precipitation rates might allow a reduction of the 0.53°C of variability in our model.

5. Conclusion

We have shown that *Pecten maximus* precipitate their shells in equilibrium with seawater when growing under natural conditions. King scallops are useful paleothermometers because (1) of the daily banding that permits the reconstruction of seasonal variations (excluding

winter) of seawater temperature at a daily scale from sea level to depths as great as 500m depth, (2) of its widespread distribution along European coasts over the past 25 millions years and (3) its stenohaline nature, which reduces reconstructed T uncertainties caused by variations in $\delta^{18}\text{O}_{\text{water}}$. Seasonal variations in temperature can be accurately predicted within $\pm 0.5^\circ\text{C}$. Knowledge of the functional biology of this organism growing in the wild has allowed us to develop a new and rigorous calibration between $\delta^{18}\text{O}$ and temperature. The robustness of this empirical calibration gives credit to the use of the *Kim and O'Neil* [1997] equation, instead of the more commonly used equation of *Epstein et al.* [1953], for attempts at reconstructing paleotemperatures from bivalve shells without a proper species specific calibration.

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Tables

Table 1.

Multiple linear regression between *Pecten* $\delta^{18}\text{O}_{\text{calcite}}$, shell growth rate, temperature in 1994, 1995 and 1996 when $\delta^{18}\text{O}_{\text{water}}$ is considered (A) or not (B).

A	Estimate	Std. Error	t-value	Pr (> t)
Intercept	4.93	0.25	19.265	<0.0001
Growth Rate (GR)	-0.0063	0.001	-4.67	<0.0001
$\delta^{18}\text{O}_{\text{Water-VSMOW}}$ (W)	-1.28	1.09	-1.177	0.24
Temperature (T)	-0.33	0.021	-15.348	<0.0001
GR*W	-0.02	0.004	-4.704	<0.0001
GR*T	0.0005	0.0001	5.093	<0.0001
W*T	0.29	0.07	3.934	<0.0001

Multiple R²: 0.93 ; Adjusted R²: 0.92 ; F-statistic: 728.4 on 6 and 325 DF; p-value: <0.0001

B	Estimate	Std. Error	t-value	Pr (> t)
Intercept	4.18	0.16	26.304	<0.0001
Growth Rate (GR)	-0.0034	0.0008	-3.94	<0.0001
Temperature (T)	-0.26	0.011	-23.289	<0.0001
GR*T	0.00025	0.00006	4.112	<0.0001

Multiple R²: 0.92 ; Adjusted R²: 0.92 ; F-statistic: 1328 on 3 and 325 DF; p-value: <0.0001

Figure Captions

Figure 1. Shell sampling location in the Bay of Brest and water sampling stations for $\delta^{18}\text{O}_{\text{water}}$ /salinity relationship in Brittany (France).

Figure 2. (A) Upper surface of the left valve of *Pecten maximus*. “Winter marks” (W_1 - W_5) deposited during spring growth restart (Chauvaud, unpublished data) are clearly visible in all individual allowing an unambiguous aging. (B) In this species daily growth increments can be observed without any treatment aside from surface cleaning (see Chauvaud et al., 1998 for details). (C) Rings or external lamellae can be counted and drilled for stable isotope determination. Individual drilled samples (raster sampling strategy) are marked with filled circles and were sampled from individuals with only one winter mark.

Figure 3. Examples of co-evolutions of shell daily growth rate (individual), bottom water temperature and $\delta^{18}\text{O}_{\text{calcite}}$ in three *Pecten maximus* individuals during one growth season in 1994, 1995 and 1996 (these data were used to build the paleotemperature equation).

Figure 4. Linear relationship between salinity and $\delta^{18}\text{O}_{\text{water-VSMOW}}$ (A) this relationship is used to calculate the mean monthly variations of $\delta^{18}\text{O}_{\text{water-VSMOW}}$ using a 30 years dataset of salinity measurements in the Bay of Brest (B).

Figure 5. Linear relationship between seawater temperature ($^{\circ}\text{C}$) and $(\delta^{18}\text{O}_{\text{calcite}} - \delta^{18}\text{O}_{\text{water}})$ where $\delta^{18}\text{O}_{\text{calcite}}$ and $\delta^{18}\text{O}_{\text{water}}$ are relative to VPDB and VSMOW, respectively.
 $T(^{\circ}\text{C}) = 14.84 - 3.75 (\delta^{18}\text{O}_{\text{calcite}} - \delta^{18}\text{O}_{\text{water}})$; $N = 333$, $R^2 = 0.92$, $p < 0.01$. Note that two values (open circles) were not taken into account in the calibration.

Figure 6. Comparison of temperature predicted with equation 8 from three individuals (shells A, B and C, year 2000, used only for validation of the paleotemperature equation) and measured instrumental temperature.

Figure 7. Comparison of temperature predicted with equations from Epstein et al. (1953), Kim and O’Neil (1997) and equation 9 (this study). Results from the three individuals (shell A, B and C, year 2000) are averaged here.

Figure 8. Relationships between $\delta^{18}\text{O}_{\text{calcite}}$ and salinity, temperature and growth rate of *P. maximus*.

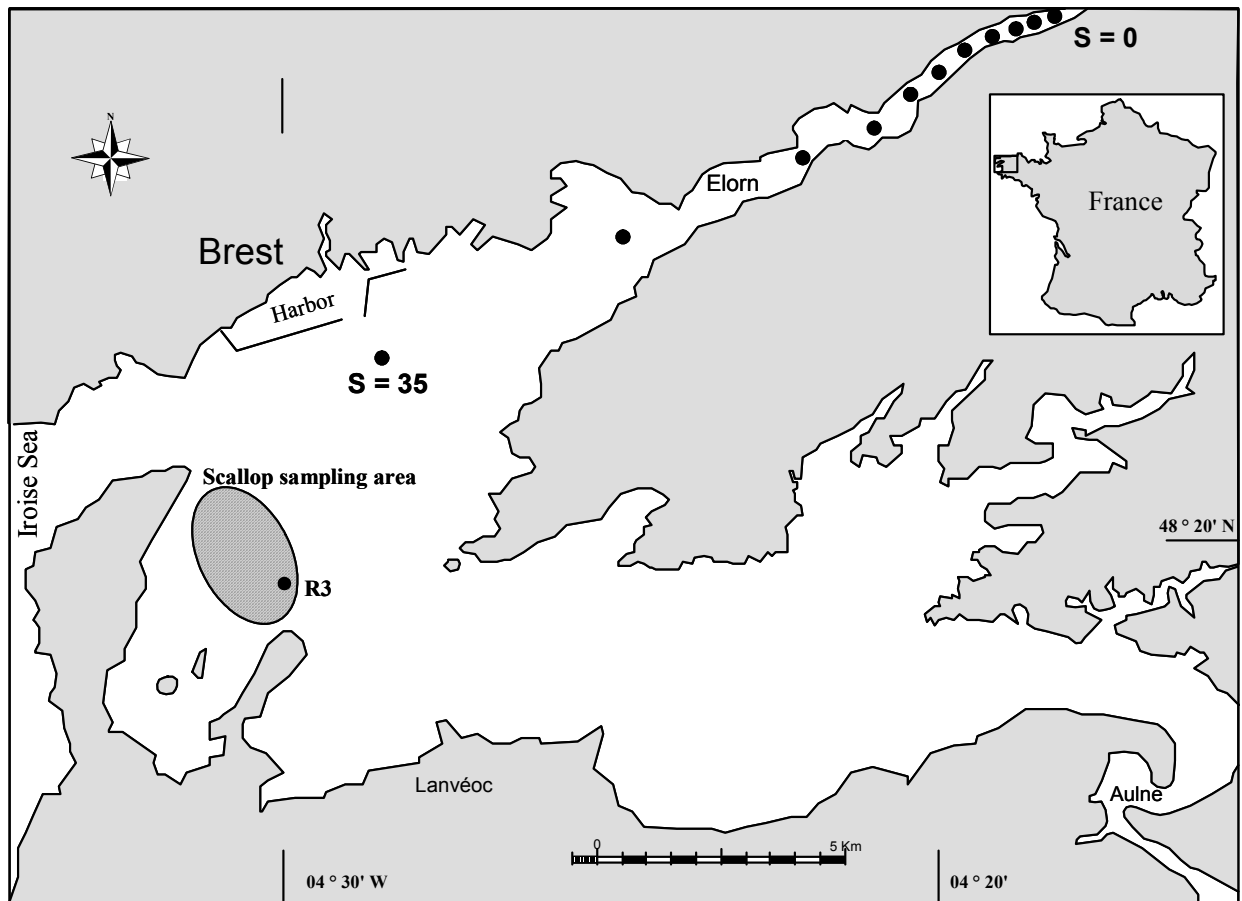
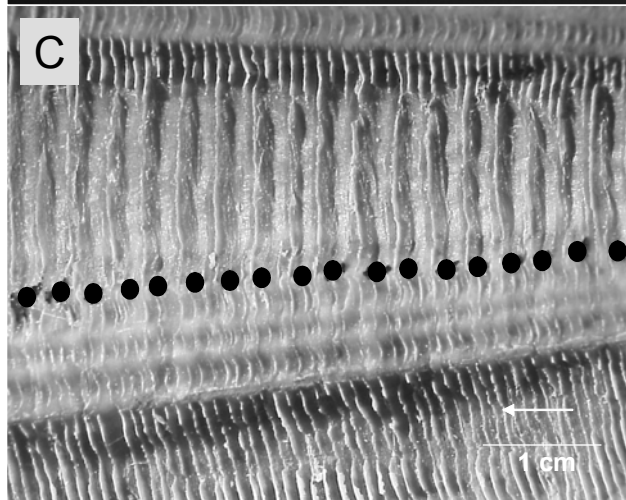
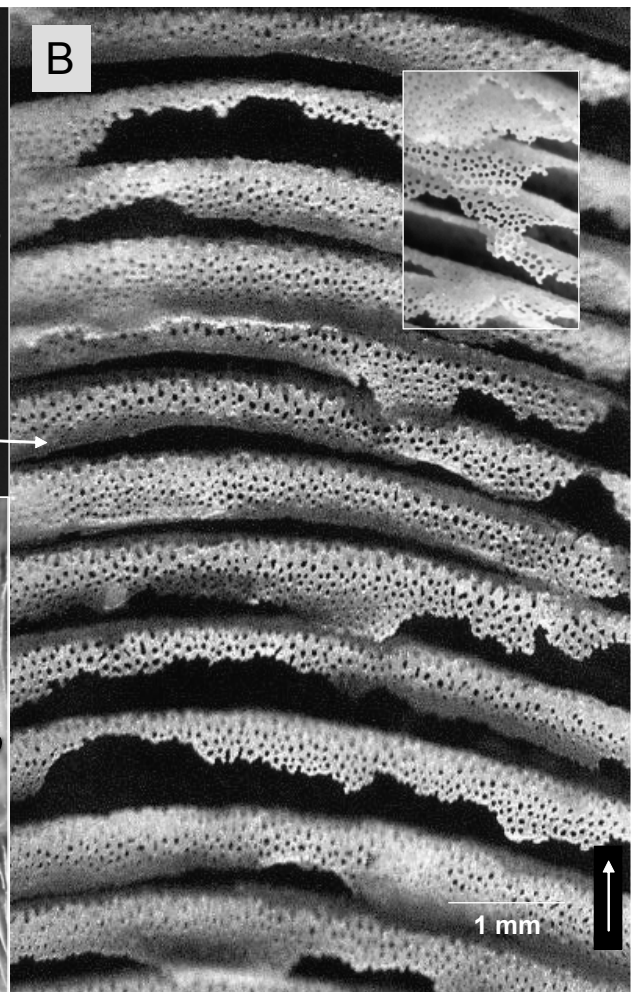
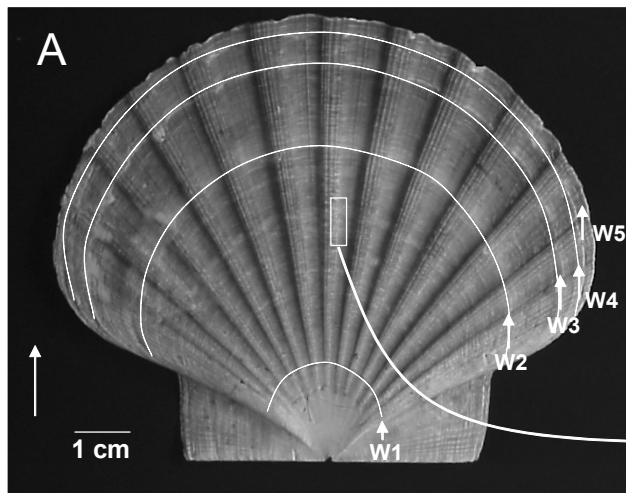


Fig. 1



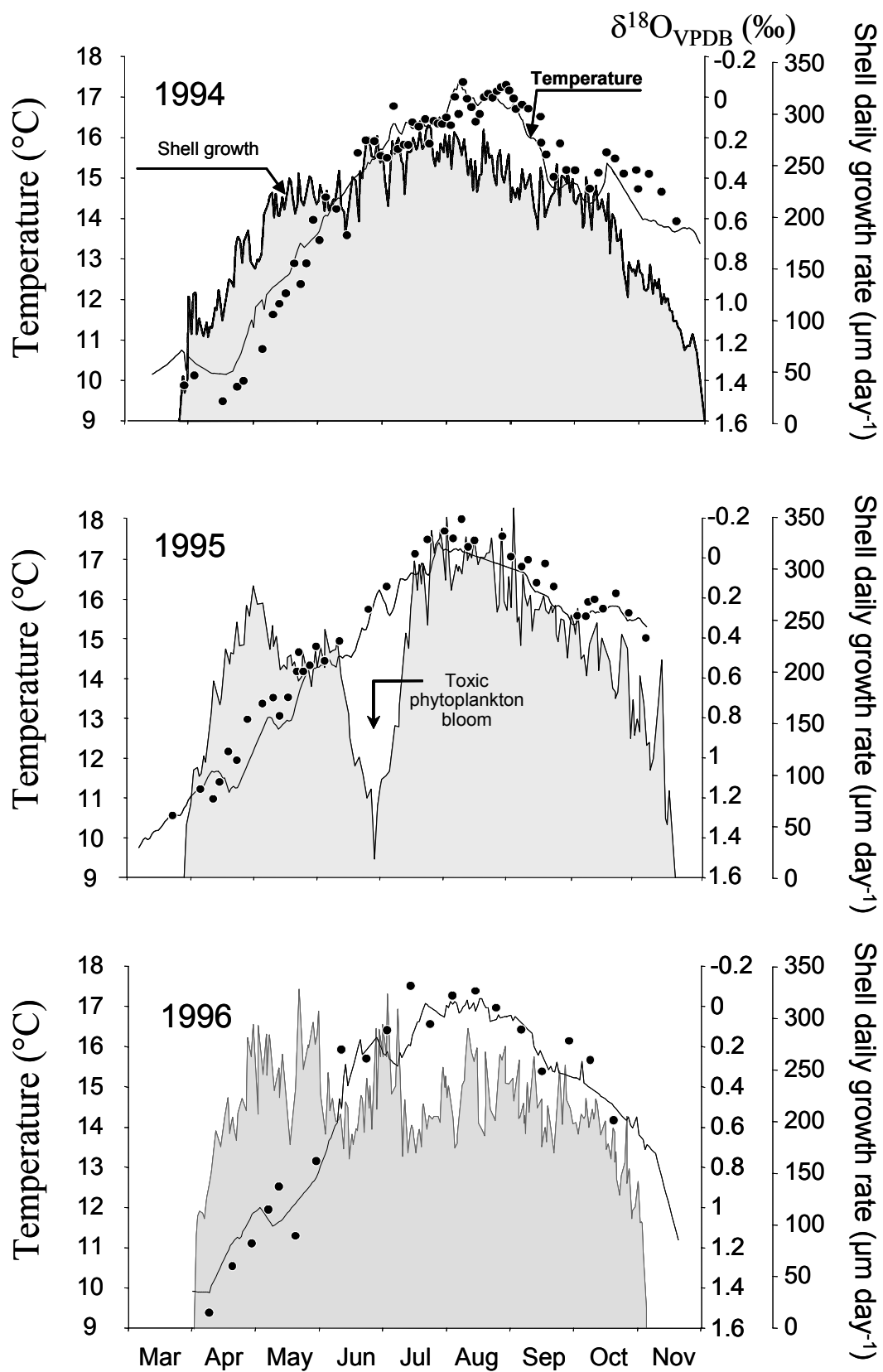


Fig 3

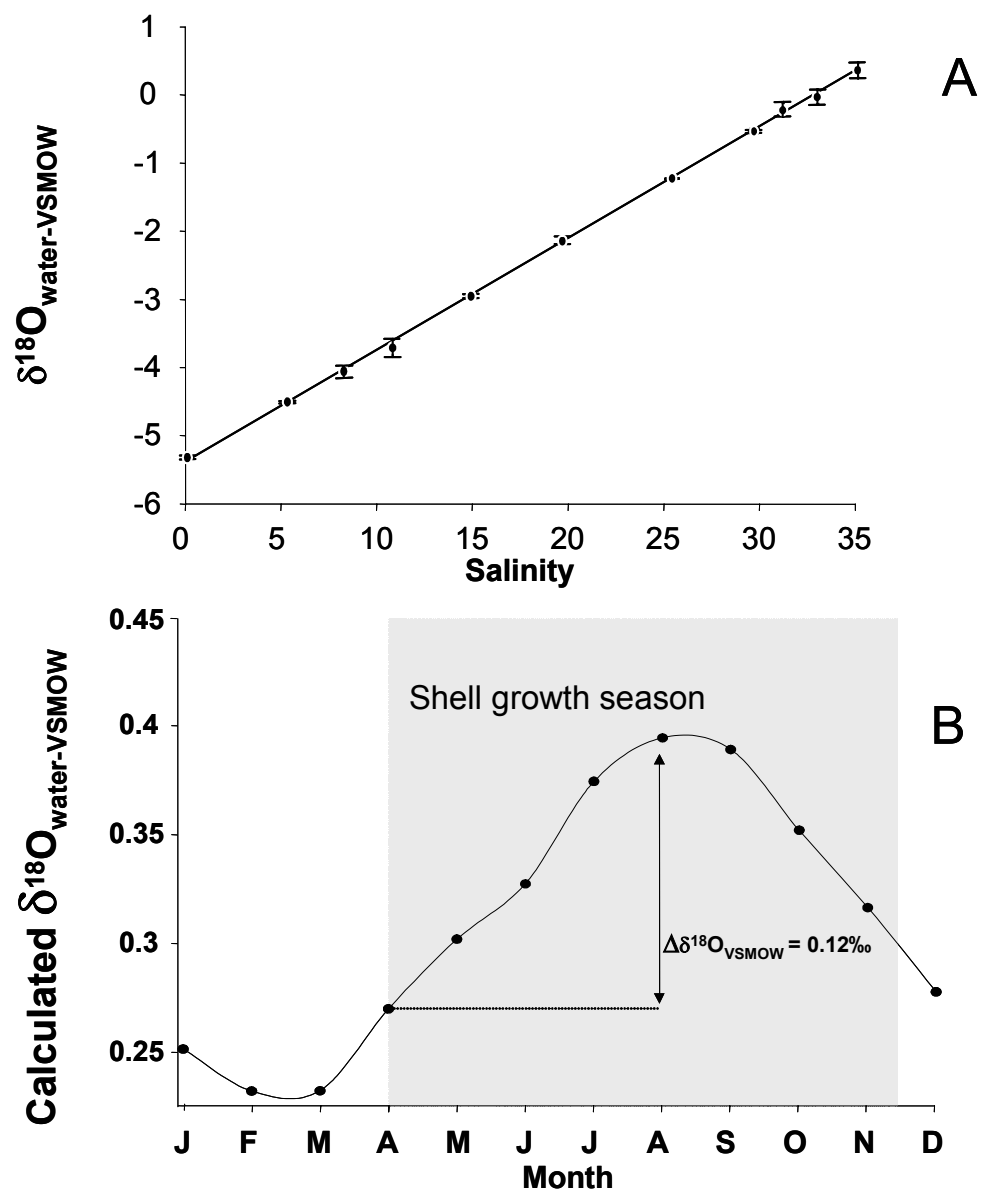


Fig.4

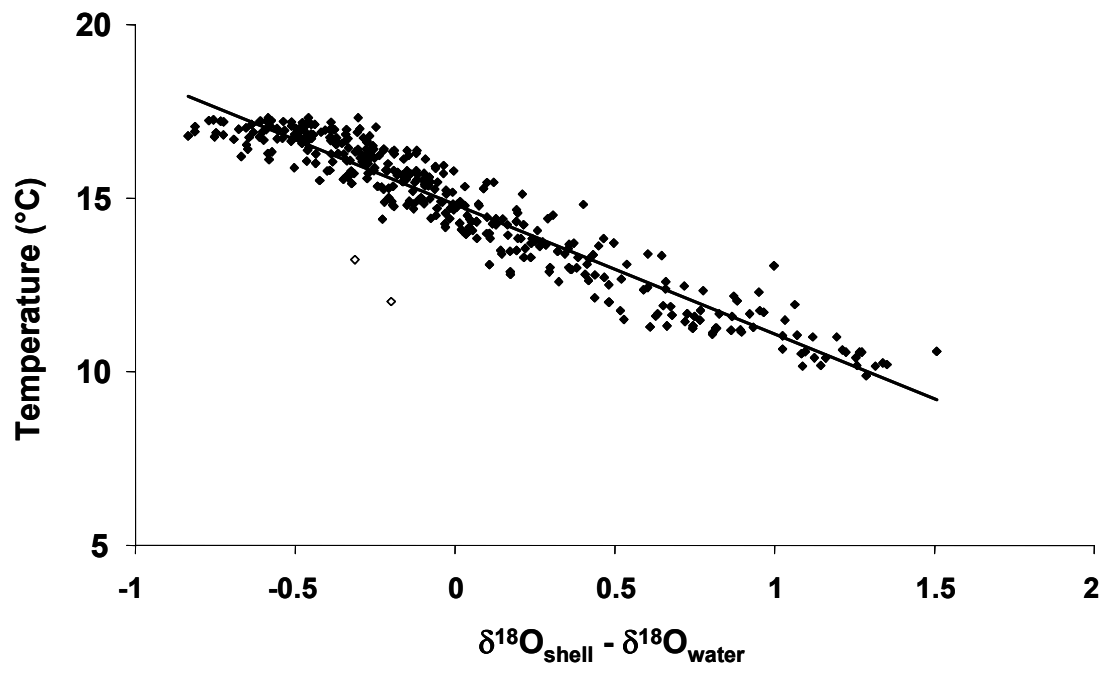


Fig.5

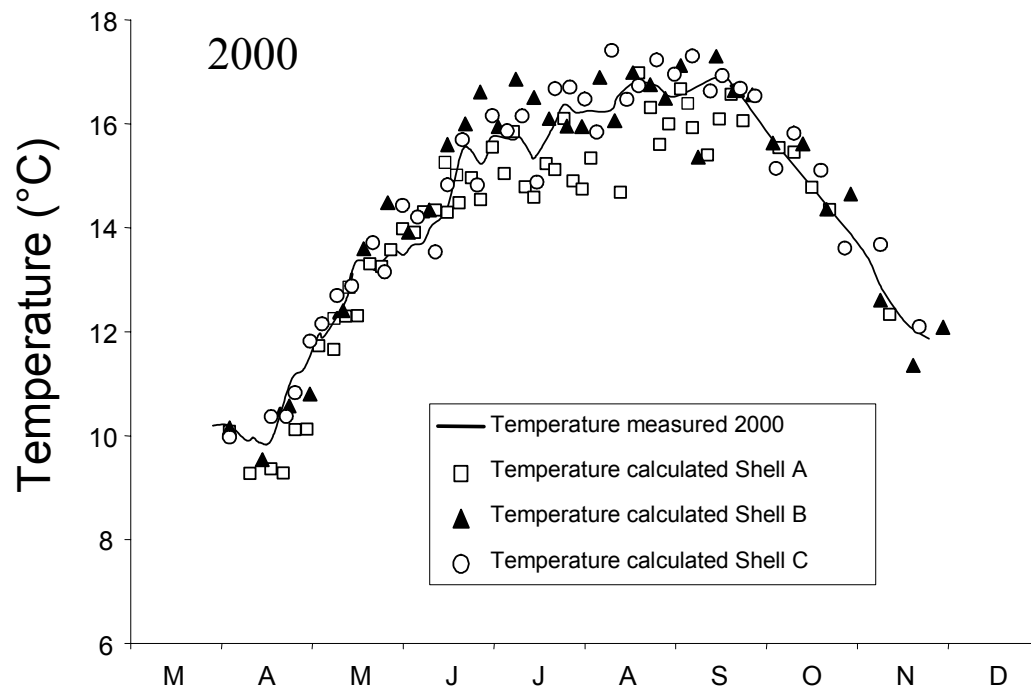


Fig. 6

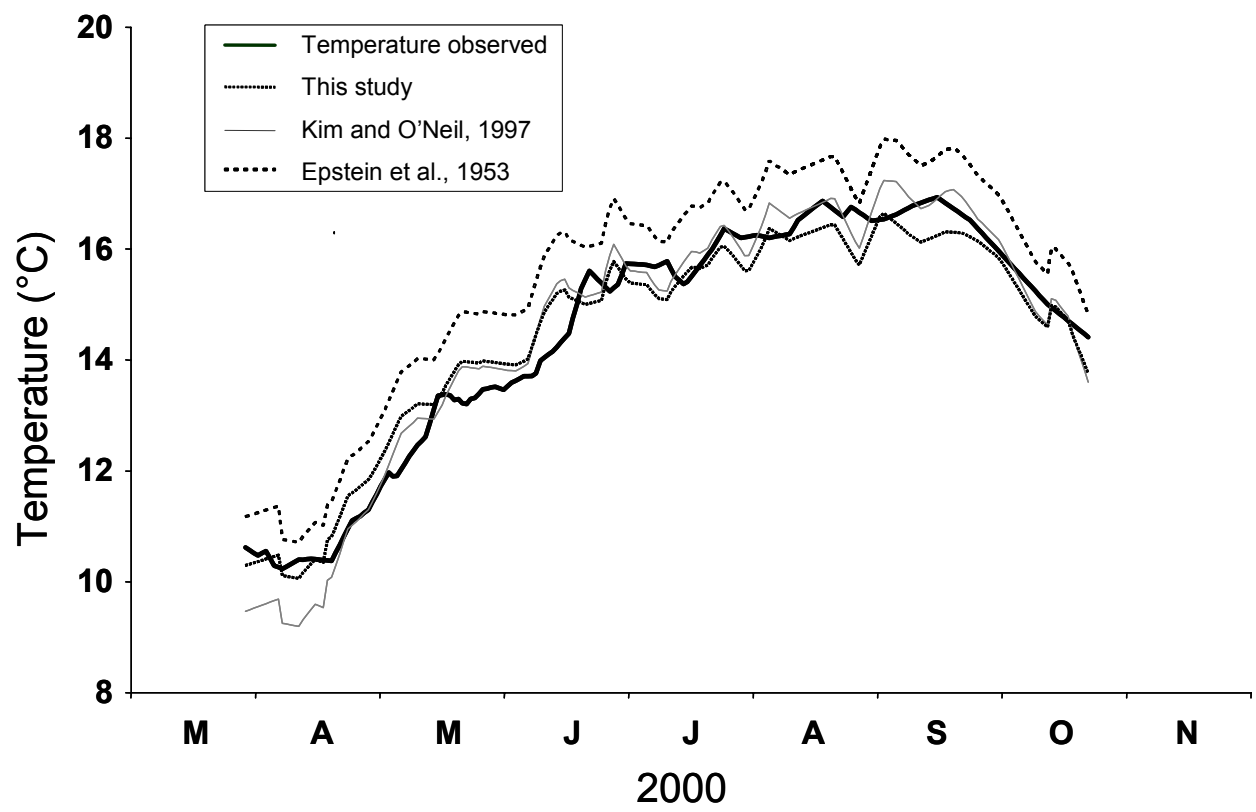


Figure 7

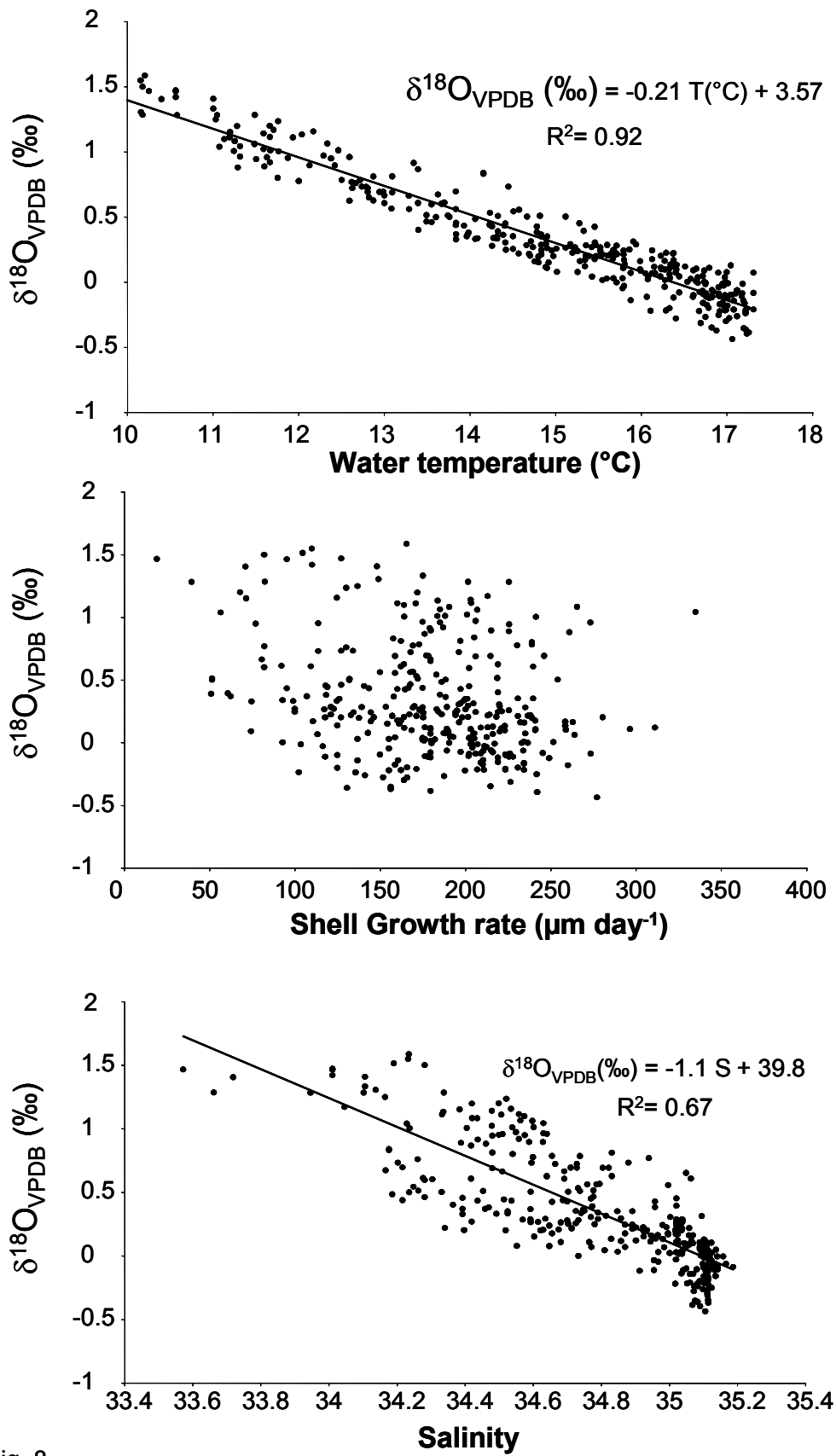


Fig. 8